

FORM PTO-1390 (Modified)
(REV 10-95)

U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER

TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371

192286US0PCT

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR

09/581560

INTERNATIONAL APPLICATION NO.
PCT/EP98/08383INTERNATIONAL FILING DATE
18 DECEMBER 1998PRIORITY DATE CLAIMED
16 JANUARY 1998

TITLE OF INVENTION

DIISOCYANATES WITH ALLOPHANATE GROUPS DERIVED FROM ALICYCLIC ALCOHOLS

APPLICANT(S) FOR DO/EO/US

Bernd BRUCHMANN, et al.

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U.S.C. 371 (c) (2))
 - a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☒ has been transmitted by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. ☒ A copy of the International Search Report (PCT/ISA/210).
8. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3))
 - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☐ have been transmitted by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☒ have not been made and will not be made.
9. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
10. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).
11. ☐ A copy of the International Preliminary Examination Report (PCT/IPEA/409).
12. ☒ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).

Items 13 to 18 below concern document(s) or information included:

13. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
14. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
15. ☒ A **FIRST** preliminary amendment.
A **SECOND** or **SUBSEQUENT** preliminary amendment.
16. ☐ A substitute specification.
17. ☐ A change of power of attorney and/or address letter.
18. ☐ Certificate of Mailing by Express Mail
19. ☒ Other items or information:

Request for Consideration of Documents Cited in International Search Report

Notice of Priority

PCT/IB/304

PCT/IB/308

Amended Sheets (pages 14, 15, 16, and 17)

| | | |
|--|--|---|
| U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR 09/581560) | INTERNATIONAL APPLICATION NO. PCT/EP98/08383 | ATTORNEY'S DOCKET NUMBER 192286US0PCT |
|--|--|---|

20. The following fees are submitted:

BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)) :

- | | |
|--|-----------------|
| <input checked="" type="checkbox"/> Search Report has been prepared by the EPO or JPO | \$840.00 |
| <input type="checkbox"/> International preliminary examination fee paid to USPTO (37 CFR 1.482) | \$670.00 |
| <input type="checkbox"/> No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO (37 CFR 1.445(a)(2)) | \$760.00 |
| <input type="checkbox"/> Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO | \$970.00 |
| <input type="checkbox"/> International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(2)-(4) | \$96.00 |

ENTER APPROPRIATE BASIC FEE AMOUNT =**CALCULATIONS PTO USE ONLY****\$840.00****\$0.00**Surcharge of **\$130.00** for furnishing the oath or declaration later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492 (e)).

| CLAIMS | NUMBER FILED | NUMBER EXTRA | RATE |
|--------------------|--------------|--------------|-----------|
| Total claims | 9 - 20 = | 0 | x \$18.00 |
| Independent claims | 1 - 3 = | 0 | x \$78.00 |

\$0.00**\$0.00****\$0.00**Multiple Dependent Claims (check if applicable). ☐**TOTAL OF ABOVE CALCULATIONS =****\$840.00**Reduction of 1/2 for filing by small entity, if applicable. Verified Small Entity Statement must also be filed (Note 37 CFR 1.9, 1.27, 1.28) (check if applicable). ☐**\$0.00****SUBTOTAL =****\$840.00**Processing fee of **\$130.00** for furnishing the English translation later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492 (f)). ☐**\$0.00****TOTAL NATIONAL FEE =****\$840.00**Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) (check if applicable). ☐**\$0.00****TOTAL FEES ENCLOSED =****\$840.00**

| | |
|---------------------------|----|
| Amount to be: refunded | \$ |
| charged | \$ |

☒ A check in the amount of **\$840.00** to cover the above fees is enclosed.☐ Please charge my Deposit Account No. _____ in the amount of _____ to cover the above fees.
A duplicate copy of this sheet is enclosed.☒ The Commissioner is hereby authorized to charge any fees which may be required, or credit any overpayment to Deposit Account No. **15-0030** A duplicate copy of this sheet is enclosed.**NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.**

SEND ALL CORRESPONDENCE TO:

**22850**

703-413-3000

WILLIAM E. BEAUMONT
REGISTRATION NUMBER 30,996

SIGNATURE

Norman F. Oblon

NAME

24,618

REGISTRATION NUMBER

DATE July 17, 2000

IN RE APPLICATION OF: Bernd BRUCHMANN, et al.

SERIAL NO.: NEW U.S. PCT APPLICATION (based on PCT/EP98/08383)

FILED: HEREWITH

FOR: DIISOCYANATES WITH ALLOPHANATE GROUPS DERIVED FROM ALICYCLIC ALCOHOLS

ASSISTANT COMMISSIONER FOR PATENTS
WASHINGTON, D.C. 20231

Sir:

Transmitted herewith is an amendment in the above-identified application.

- ☒ No additional fee is required.
- ☐ Small entity status of this application under 37 C.F.R. §1.9 and §1.27 has been established by a verified statement previously submitted.
- ☐ Small entity status of this application under 37 C.F.R. §1.9 and §1.27 has been established by a verified statement submitted herewith.
- ☒ Additional documents filed herewith: English Translation of Specification/Declaration/Notice of Priority Check for \$840.00/PCT/IB/304/Preliminary Amendment/PCT/IB/308/International Search Report Request for Consideration/Amended Pages (14, 15, 16, and 17)/PCT Transmittal Letter

The fee has been calculated as shown below.

| (Col. 1) | | (Col. 2) | | (Col. 3) | SMALL ENTITY | | OTHER THAN A SMALL ENTITY | |
|---|---------------------------|----------|--|------------------|--------------|-------------------|---------------------------|-------------------|
| | CLAIMS REMAINING AFTER | | HIGHEST NUMBER PREVIOUSLY PAID FOR | PRESENT EXTRA | RATE | ADDITIONAL FEE | RATE | ADDITIONAL FEE |
| TOTAL | * 9 | MINUS | ** 20 | = 0 | X9 = | \$ | X18 = | \$.00 |
| INDEP | * 1 | MINUS | *** 3 | = 0 | X39 = | \$ | X78 = | \$.00 |
| <input type="checkbox"/> FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM | | | | | +130= | \$ | +260= | \$ |
| TOTAL | | | | | | \$ | TOTAL | \$.00 |

A check in the amount of \$_____ is attached.

- XX Please charge any additional fees for the papers being filed herewith and for which no check is enclosed herewith, or credit any overpayment to deposit Account No. 15-0030. A duplicate copy of this sheet is enclosed.
- XX If these papers are not considered timely filed by the Patent and Trademark Office, then a petition is hereby made under 37 C.F.R. §1.136, and any additional fees required under 37 C.F.R. §1.136 for any necessary extension of time may be charged to deposit Account No. 15-0030. A duplicate copy of this sheet is enclosed.

OBLON, SPIVAK, McCLELLAND,
MAIER & NEUSTADT, P.C.

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Norman F. Oblon
Attorney of Record
Registration No. 24,618
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Registration No. 34,423

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- *If the entry in Column 2 is less than the entry in Column 1 write "0" in Column 3.
- **If the "Highest Number Previously paid for" IN THIS SPACE is less than 20 write "20" in this space.
- ***If the "Highest Number Previously paid for" IN THIS SPACE is less than 3 write "3" in this space.

192286US0PCT

09/581560
534 Rec'd PCT/PTC 17 JUL 2000

IN THE UNITED STATES PATENT & TRADEMARK OFFICE

IN RE APPLICATION OF :

BERND BRUCHMANN ET AL. :

SERIAL NO: NEW US PCT APPLICATION : ATTN: APPLICATION BRANCH
BASED ON PCT/EP98/08383

FILED: HEREWITH :

FOR: DIISOCYANATES WITH ALLO-
PHANATE GROUPS DERIVED
FROM ALICYCLIC ALCOHOLS

PRELIMINARY AMENDMENT

ASSISTANT COMMISSIONER FOR PATENTS
WASHINGTON, D.C. 20231

SIR:

Prior to examination on the merits, please amend the above-identified application as follows.

IN THE CLAIMS

Please amend the claims as follows:

Claim 2, line 1, change "A" to --The--.

Claim 3, line 1, change "A" to --The--, same line, delete "or 2".

Claim 4, line 1, change "A" to --The--, same line, change "any of claims 1 to 3" to
--Claim 1--.

Claim 5, line 1, change "A" to --The--;

lines 1-2, change "any of claims 1 to 4" to --Claim 1--.

002129"095T8560

Claim 6, line 1, change "A" to --The--.

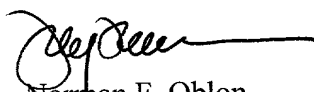
REMARKS

Claims 1-9 are active in the present application. The claims are amended for clarity and to remove multiple dependencies. No new matter has been added.

Applicants submit that the present application is now in a condition for examination on the merits. Early notice of such is earnestly solicited.

Respectfully submitted,

OBLON, SPIVAK, McCLELLAND,
MAIER & NEUSTADT, P.C.



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WILLIAM E. BEAUMONT
REGISTRATION NUMBER 30,996

09/581560

DOCKET NO.: 192286US0PCT

534 Rec'd PCT/PTC 17 JUL 2000

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

IN RE APPLICATION OF: Bernd BRUCHMANN, et al.

SERIAL NO.: NEW U.S. PCT APPLICATION

FILED: HEREWITH

INTERNATIONAL APPLICATION NO.: PCT/EP98/08383

INTERNATIONAL FILING DATE: 18 DECEMBER 1998

FOR: DIISOCYANATES WITH ALLOPHANATE GROUPS DERIVED FROM
ALICYCLIC ALCOHOLS**REQUEST FOR PRIORITY UNDER 35 U.S.C. 119**
AND THE INTERNATIONAL CONVENTIONAssistant Commissioner for Patents
Washington, D.C. 20231

Sir:

In the matter of the above-identified application for patent, notice is hereby given that the applicant claims as priority:

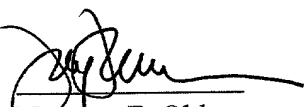
| <u>COUNTRY</u> | <u>APPLICATION NO</u> | <u>DAY/MONTH/YEAR</u> |
|----------------|-----------------------|-----------------------|
| GERMANY | 198 01 322.1 | 16 JANUARY 1998 |

Certified copies of the corresponding Convention application(s) were submitted to the International Bureau in PCT Application No. **PCT/EP98/08383**. Receipt of the certified copy(s) by the International Bureau in a timely manner under PCT Rule 17.1(a) has been acknowledged as evidenced by the attached PCT/IB/304.

Respectfully submitted,
OBLON, SPIVAK, McCLELLAND,
MAIER & NEUSTADT, P.C.



22850


Norman F. Oblon
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Surinder Sachar
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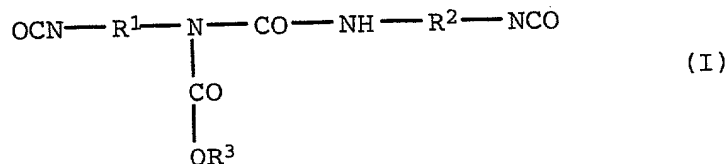
WILLIAM E. BEAUMONT
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534 Rec'd PCT/PTC 17 JUL 2000

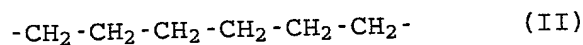
Diisocyanates with allophanate groups derived from alicyclic alcohols

5 The present invention relates to diisocyanates of the formula (I)



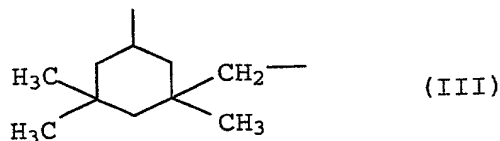
10 in which the radicals have the following meanings:

R^1, R^2 : both radicals a radical of the formula (II)



(diisocyanates Ia)

20 one radical a radical of the formula (II) and the other radical a radical of the formula (III)



(diisocyanates Ib)

both radicals a radical of the formula (III) (diisocyanates Ic),

30 R^3 : - a 5- or 6-membered cycloalkyl radical in which up to 3 hydrogen atoms may be substituted by C_1 - C_4 -alkyl radicals and one or two methylene units may be substituted by an oxygen atom and/or a tertiary nitrogen atom which additionally

35 carries a C_1 - C_4 -alkyl radical, or

- a C_1 - C_4 -alkyl radical in which one hydrogen atom is substituted by a 5- or 6-membered cycloalkyl radical in which up to 3 hydrogen atoms may be substituted by C_1 - C_4 -alkyl radicals and one or two methylene units may be substituted by an oxygen atom and/or a tertiary nitrogen atom which additionally carries a C_1 - C_4 -alkyl radical; a pyrrolidone radical or a morpholine radical, where in the case of the two last-mentioned radicals the nitrogen atom is attached to the

40

45 alkyl radical.

The invention additionally relates to isocyanate mixtures and to 2-component coating compositions which comprise these isocyanates; coating processes in which these 2-component coating compositions are employed, and the coated articles produced by these processes.

Crosslinking polyisocyanates and binder components having isocyanate-reactive groups are generally known in the form, for example, of 2-component coating materials (cf. Kunststoff Handbuch, Volume 7, Polyurethane, 2nd Edition, 1983, Carl Hanser Verlag Munich Vienna, pp. 540-561). These 2-component coating compositions comprise as their binder, for example, a polymeric polyol and, as their crosslinker component (hardener), a compound having two or more free isocyanate groups.

- 15 The service properties of coating materials whose polymeric binders have been crosslinked with the isocyanates are much better than those of systems comprising low molecular mass binders. This relates in particular to service properties such as
- 20 - insensitivity to mechanical exposure such as tension, strain, impact or abrasion
- 25 - resistance to moisture (in the form of water vapor, for example) and to dilute chemicals
- resistance to environmental influences, such as temperature fluctuations and UV radiation
- 30 - high gloss of the coated surfaces.

The hardeners (curing agents) are expected not only to give the cured coatings the abovementioned service properties but also to improve, or at least have very little adverse effect on, the processing properties of the coating materials prior to their application.

So that the coating materials can be applied without problems by customary techniques - for example, by spraying them onto the surface to be coated - the coating materials are intended to possess a certain viscosity. Consequently, 2-component coating compositions normally comprise solvents. The high solvent content of these coating materials itself causes problems, however, since the coating-material processors are forced to take complex measures to avoid atmospheric emission of the solvents, which are released when the coating materials are applied and dried. The search has therefore been on for hardeners which do not greatly

increase the viscosity of the binder-containing component or which, even better, reduce it. These hardeners themselves of course must not display any notable volatility at room temperature, as is the case with customary commercial monomeric isocyanates such as hexamethylene diisocyanate or isophorone diisocyanate.

In addition, following their application the 2-component coating compositions should cure as rapidly as possible so that the coated articles, following application, can be subjected rapidly to further processing or use.

Polyisocyanates comprising allophanate groups and biuret groups are known, for example, from EP-A-496 208, 524 501 and 566 037, where they are recommended for use as hardeners in 2-component coating systems. Structural components include aliphatic monoalcohols and all customary isocyanates. The structural components from the group of the cyclic monoalcohols, and hexamethylene diisocyanate and isophorone diisocyanate, are present in these documents only in the context of lists of the appropriate isocyanate and alcohol components. As evident from the experimental section of these documents, the focus is on polyisocyanates having allophanate and biuret groups which are derived from noncyclic alcohols.

The allophanates derived from these alcohols have the disadvantage, in particular, that the 2-component coating systems prepared therewith are relatively slow to cure and even following complete curing still have a level of surface hardness which is inadequate for many applications.

DE-A-42 29 183 discloses urethane- and isocyanurate-functional polyisocyanates of low viscosity. They are prepared by reacting, for example, cycloaliphatic alcohols, such as cyclohexanol, with an isocyanurate of hexamethylene diisocyanate to give the corresponding urethane.

Although the properties of the hardeners disclosed therein satisfy in most respects the customary requirements placed on the processing properties of the uncured liquid systems which comprise these hardeners and on the service properties of the coatings produced with the coating materials, the hardeners nevertheless still appear to be in need of improvement in terms of the viscosity of the coating systems, their curing rate, and the hardness of the coatings produced therewith.

It is an object of the invention to provide this improvement.

We have found that this object is achieved by the compounds of the formula (I) defined at the outset, by mixtures and

- 5 2-component coating compositions which comprise these compounds and by articles which are coated with these 2-component coating compositions.

The diisocyanates of the formula (I) according to the invention
10 are derived preferably from alcohols such as cyclohexanol, cyclohexanemethanol, cyclopentanol, cyclopentanemethanol, 3,3,5-trimethylcyclohexanol, menthol, norborneol, N-methyl-4-hydroxypiperidine, 4-(2-hydroxyethyl)morpholine or 4-(2-hydroxyethyl)pyrrolidone.

15

These diisocyanates can generally be prepared by reacting

- (i) isophorone diisocyanate (IPDI), hexamethylene diisocyanate (HDI) or a mixture of these isocyanates in the presence of
20 a catalyst with a
- 5- or 6-membered cycloaliphatic alcohol in which up to 3 hydrogen atoms attached to one carbon atom may be substituted by C₁-C₄-alkyl radicals and one or two methylene units may be substituted by an oxygen atom and/or a tertiary nitrogen atom which additionally carries a C₁-C₄-alkyl radical, or
25
 - C₁-C₄-alkyl alcohol in which one hydrogen atom attached to a carbon atom is substituted by a 5- or 6-membered cycloalkyl radical in which up to 3 hydrogen atoms may be substituted by C₁-C₄-alkyl radicals and one or two methylene units may be substituted by an oxygen atom and/or a tertiary nitrogen atom which additionally carries a C₁-C₄-alkyl radical; a pyrrolidone radical or morpholine radical, where in the case of the two
30 35 last-mentioned radicals, the nitrogen atom is attached to the alkyl radical of the alcohol;
- 40 the molar ratio of said isocyanates to said monoalcohol being from 1.5:1 to 20:1,
- (ii) deactivating the catalyst and
- 45 (iii) removing any unreacted isocyanate.

The molar mixing ratio of the HDI/IPDI mixtures is preferably from 0.1:1 to 10:1.

The reaction can be performed, for example, in the way described in EP-A-524 501.

Examples of the catalysts used are quaternary ammonium salts, an example being N,N,N-trimethyl-N-(2-hydroxypropyl)ammonium 2-ethylhexanoate.

10

The reaction is generally conducted at temperatures from 50 to 150°C.

The reaction is ended by cooling the reaction mixture and removing the catalyst, subjecting it to thermal decomposition or adding a suitable agent which deactivates the catalyst. Examples of suitable such agents are acids such as p-toluenesulfonic acids, dibutyl phosphate, or di(2-ethylhexyl) phosphate.

20 After the end of the reaction, unreacted hexamethylene diisocyanate or isophorone diisocyanate is generally removed by distillation, preferably down to a content of less than 0.5% by weight.

25 The reaction product, which is essentially free from isophorone diisocyanate or hexamethylene diisocyanate, has a viscosity of generally from 100 to 10,000, preferably from 150 to 6000 mPas, measured in accordance with ISO 3219.

30 This method generally produces mixtures which may comprise, in addition to the diisocyanates (Ia), (Ib) and/or (Ic),

- urethanes of the formula (IV)

35
$$\text{OCN-R}^1\text{-NH-CO-OR}^3 \quad (\text{IV})$$

in which the radicals R^1 and R^3 may have the following meanings:

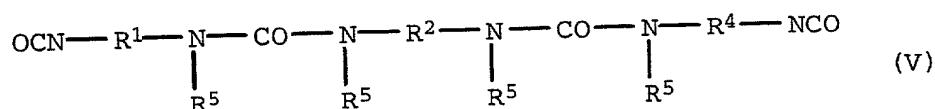
40 R^1 : a radical of the formula (II) or (III),

R^3 : the meaning indicated in claim 1;

- diisocyanates of the formula (V)

45

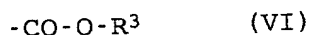
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5 in which the radicals R^1 , R^2 , R^4 and R^5 may have the following meanings:

R^1 , R^2 , R^4 : the meaning indicated for R^1 in formula (I),

10 R^5 : 2 of the total of 4 radicals are hydrogen and the other two radicals are a radical of the formula (VI)



15 with the radicals R^5 having the same meaning being separated by the unit R^2 ; and

- isocyanurates composed of 3 molecules selected from the group
20 consisting of isophorone diisocyanate and hexamethylene diisocyanate.

Generally, in these mixtures

25 - the sum proportion of the diisocyanates (Ia), (Ib) and (Ic) is from 5 to 100% by weight,

- the proportion of the urethanes of the formula (IV) is from 0 to 20% by weight,

30 - the proportion of the diisocyanates of the formula (V) is from 0 to 30% by weight and

- the proportion of the isocyanurates each composed of
35 3 molecules selected from the group consisting of isophorone diisocyanate and hexamethylene diisocyanate is from 0 to 65% by weight.

Preferably, the weight ratio of diisocyanates (I) to monoiso-
40 cyanurates (VII) is from 10:1 to 1:10.

Preferably, the sum of the proportions of the diisocyanates (Ia), (Ib), (Ic), (V), the urethane (IV) and the isocyanurate (VII) is from 10 to 100% by weight.

45

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If desired, the diisocyanates of the invention can easily be isolated from these mixtures by known separation methods such as gel permeation chromatography. Generally, however, this is unnecessary insofar as these diisocyanates (Ia), (Ib) and (Ic) are employed in the form of the abovementioned mixtures as crosslinkers in 2-component polyurethane coating compositions. The diisocyanates (Ia), (Ib) and (Ic) and the abovementioned mixtures comprising these diisocyanates are particularly suitable as component B in the preparation of 2-component coating compositions which as component A comprise a compound which carries polyisocyanate-reactive groups, preferably a hydroxy-functional polymer (A).

The hydroxy-functional polymers (A) are, for example, polymers having a hydroxyl group content of from 0.1 to 20% by weight, preferably from 0.5 to 10% by weight. The number-average molecular weight M_n of the polymers is preferably from 1000 to 100,000, and with particular preference from 2000 to 10,000. The polymers concerned are preferably those which consist to the extent of more than 50% by weight of C_1 - C_{20} -alkyl (meth)acrylate, vinylaromatic compounds having up to 20 carbon atoms, vinyl esters of carboxylic acids containing up to 20 carbon atoms, vinyl halides, nonaromatic hydrocarbons having 4 to 8 carbon atoms and 1 or 2 double bonds, unsaturated nitriles and mixtures thereof. Particular preference is given to those polymers which consist to the extent of more than 60% by weight of C_1 - C_{10} -alkyl (meth)acrylates, styrene or mixtures thereof.

The polymers (A) may additionally comprise hydroxy-functional monomers in accordance with the above hydroxyl group content and, if desired, further monomers, examples being ethylenically unsaturated acids, especially carboxylic acids, acid anhydrides or acid amides.

Examples of further polymers (A) are polyesterols, as are obtainable by condensing polycarboxylic acids, especially dicarboxylic acids, with polyols, especially diols.

Further suitable polymers (A) are polyetherols, which are prepared by addition reaction of ethylene oxide, propylene oxide or butylene oxide onto H-active components. Polycondensates of butanediol are likewise suitable.

The polymers (A) can of course also comprise compounds having primary or secondary amino groups.

By way of example there may be mentioned products known as Jeffamines, i.e. amino-terminated polyetherols or oxazolidines.

- In addition to the components A and B set out above, the
- 5 2-component coating compositions may also comprise other polyisocyanates and compounds having polyisocyanate-reactive groups, as are normally present in 2-component coating compositions.
- 10 The molar ratio formed from the sum of the isocyanate groups in the components B to the sum of the isocyanate-reactive groups of component (A) is preferably from 0.6:1 to 1.4:1, particularly preferably from 0.7:1 to 1.3:1 and, with very particular preference, 1:1.
- 15 The coating compositions of the invention may additionally comprise organic solvents, examples being xylene, butyl acetate, methyl isobutyl ketone, methoxypropyl acetate, N-methyl-pyrrolidone. Solvents are used to establish the low viscosity
- 20 which is desired for the processing of the coating composition, i.e. for its application to substrates.
- The coating compositions may of course include further additives customary in coatings technology, examples being pigments,
- 25 fillers, leveling assistants, etc.
- They may also contain catalysts for urethane formation, such as dibutyltin dilaurate.
- 30 The 2-component polyurethane coating compositions can be prepared in a known manner. Normally, components A and B are mixed before the coating compositions are applied to a substrate. Mixing takes place normally from 0 to 8 h before application. The desired viscosity can be established with solvents.
- 35 The polyurethane coating compositions can be applied in a customary manner by spraying, pouring, rolling, brushing, knife-coating, etc., in a sheetlike manner to substrates.
- 40 The coating compositions are particularly suitable for workpieces with surfaces made from metal, plastic, wood, woodbase materials or glass.

The articles coated by these processes feature a surface which

45 has very good mechanical properties - in particular, good hardness, flexibility and chemical resistance. With the coating

compositions of the invention, these properties are achieved after only a particularly short curing time.

Experimental section

5

A. Preparing the urethane- and allophanate-functional polyisocyanates

10 A.1 Preparing the urethane- and allophanate-functional polyisocyanates from HDI and monoalcohols, and comparative examples

15 Hexamethylene diisocyanate (HDI) was charged to a reaction vessel, under a nitrogen blanket, and the amount of OH component indicated in Table 1 was added. The mixture was heated to 80°C, 200 ppm by weight (based on diisocyanate) of the catalyst, N,N,N-trimethyl-N-(2-hydroxypropyl) ammonium 2-ethylhexanoate, were added, reaction was allowed to take place at this temperature, and the reaction was stopped on reaching the NCO content specified in Table 1 by adding 20 250 ppm by weight (based on diisocyanate) of di(2-ethylhexyl) phosphate. The reaction mixture was subsequently distilled in a thin-film evaporator at an oil temperature of 165°C and under 2.5 mbar in order to remove monomeric HDI. The residual content of HDI monomer was then below 0.2% by weight. 25

Data for the end products are given in Table 1.

30 A.2 Preparing a urethane- and allophanate-functional polyisocyanate from IPDI and cyclohexanol

35 6 mol of IPDI were charged to a reaction vessel, under a nitrogen blanket and 1.2 mol (20 mol%) of cyclohexanol were added. The mixture was heated to 70°C, 800 ppm by weight (based on diisocyanate) of the catalyst specified in A.1 were added, reaction was allowed to take place at this temperature and the reaction was stopped at an NCO content of the mixture of 27% by weight by adding 1000 ppm by weight (based on diisocyanate) of di(2-ethylhexyl)phosphate. The reaction 40 mixture was subsequently distilled in a thin-film evaporator at an oil temperature of 165°C and under 2.5 mbar in order to remove monomeric IPDI.

45 The solid end product had an NCO content of 15.4% and a softening point at 43°C.

A.3 Preparing a urethane- and allophanate-functional polyisocyanate from an IPDI/HDI mixture and cyclohexanol.

5 A mixture of 4 mol of HDI and 1.5 mol of IPDI was charged to a reaction vessel, under a nitrogen blanket, and 1.1 mol (20 mol%) of cyclohexanol were added. The mixture was heated to 80°C, 650 ppm by weight (based on diisocyanate) of N,N,N-trimethyl-N-(2-hydroxypropyl)ammonium 2-ethylhexanoate were added, reaction was allowed to take place at this
10 temperature, and the reaction was stopped at an NCO content of the mixture of 31% by weight by adding 800 ppm by weight (based on diisocyanate) of di(2-ethylhexyl) phosphate. The reaction mixture was subsequently distilled in a thin-film evaporator at an oil temperature of 165°C and under 2.5 mbar
15 in order to remove monomeric IPDI.

The end product had an NCO content of 17.1% and a viscosity at 25°C of 4310 mPas.

20 B. Production and testing of clearcoats from the polyisocyanates of the invention

By way of example, the polyisocyanates of the invention were mixed with a hydroxy-functional acrylate resin (Lumitol®
25 H 136, BASF) and with various polyisocyanate hardeners (comparison coating material 1: Basonat® HI 100, BASF, comparison coating material 12: allophanate based on HDI with 20 mol% ethylhexanol) in accordance with stoichiometric OH/NCO proportions, and if required was catalyzed with dibutyltin dilaurate (DBTL, Merck) in order to accelerate curing.
30 Adjustment to an application viscosity of 20 s (DIN 53 211 cup 4 mm flow nozzle) was made with butyl acetate. The processing times (potlives) of the coating materials were adjusted by way of the amount of catalyst added in such a way
35 that drying times of about 1 h were attained. Coatings with a wet film thickness of 200 µm were applied to glass plates using a film-drawing frame. The resulting clearcoats were cured under standard climatic conditions for 7 days. The solids contents were determined in accordance with
40 DIN V 53 216 Part 1.

The coating materials prepared with the crosslinkers of the invention have improved solids contents and a lower
45 proportion of volatile organic constituents (VOC) relative to a standard isocyanate (coating material No. 1 compar.). This means that in order to obtain coating materials having the same viscosity, less solvent is required in the case of the

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coating materials prepared with the isocyanates of the invention.

5 Relative to an allophanate synthesized from noncycloaliphatic alcohols, the coating materials of the invention have a much higher initial hardness and ultimate hardness (cf. Tab. 4, coating material No. 12 (comparative expt.) with the coating materials of the invention). When N-alkylhydroxypiperidine is used, moreover, it is unnecessary to add a catalyst to cure the coating compositions.

10 All coating materials, moreover, display good flexibility, good adhesion and good scratch resistance.

15 Table 1: Reaction products of HDI and monoalcohols

| Experiment No. | Monoalcohol | Amount based on isocyanate (mol %) | NCO content of the mixture (% by wt.) | NCO content after distillation (% by wt.) | Viscosity at 25°C (mPas) | |
|----------------|------------------|------------------------------------|---------------------------------------|---|--------------------------|------|
| 20 | 1 | Cyclohexanol | 5 | 40.2 | 20.7 | 1220 |
| | 2 | Cyclohexanol | 10 | 36.9 | 19.5 | 1120 |
| | 3 | Cyclohexanol | 15 | 35.7 | 18.3 | 890 |
| | 4 | Cyclohexanol | 20 | 34.1 | 17.4 | 770 |
| | 5 | Cyclopentanol | 5 | 40.1 | 21.0 | 980 |
| | 6 | Cyclopentanol | 10 | 38.2 | 19.8 | 660 |
| 25 | 7 | Cyclopentanol | 15 | 36.8 | 18.3 | 610 |
| | 8 | Cyclopentanol | 20 | 34.6 | 17.1 | 650 |
| | 9 | Cyclohexanemethanol | 20 | 35.8 | 16.0 | 360 |
| | 10 | Cyclopentanemethanol | 20 | 35.0 | 18.6 | 560 |
| | 11 | 3,3,5-Trimethylcyclohexane | 10 | 36.2 | 18.3 | 1830 |
| 30 | 12 | 3,3,5-Trimethylcyclohexane | 20 | 32.2 | 15.9 | 1620 |
| | 13 | Menthol | 20 | 34.6 | 14.5 | 1330 |
| | 14 | Norborneol | 10 | 35.8 | 19.0 | 1810 |
| | 15 | Norborneol | 20 | 33.0 | 16.9 | 1320 |
| | 16 | N-Methyl-4-hydroxypiperidine | 10 | 36.0 | 12.9 | 1320 |
| 35 | 17 | N-Methyl-4-hydroxypiperidine | 20 | 29.0 | 10.0 | 3340 |
| | 18 | 4-(2-Hydroxyethyl)-morpholine | 5 | 39.1 | 18.3 | 4550 |
| | 19 | 4-(2-Hydroxyethyl)-morpholine | 20 | 28.1 | 15.3 | 3580 |
| 40 | 20 | N-(2-Hydroxyethyl)-2-pyrrolidone | 20 | 32.3 | 16.2 | 2020 |
| | 21 (comparative) | n-Butanol | 20 | 33.5 | 18.3 | 273 |
| | 22 (comparative) | 2-Ethylhexanol | 20 | 31.2 | 16.5 | 343 |

Table 2: Improved VOC values relative to the prior art

| | | | | | | | | |
|----|--------------------------------------|-------------|---------------|-------|-------|--------------|-------|-------|
| 5 | Coating composition | | | | | | | |
| | Coating material | 1 (compar.) | 2 | 3 | 4 | 5 | 6 | 7 |
| | Polyisocyanate (Tab. 1) | HI 100 | 5 | 6 | 7 | 1 | 2 | 3 |
| | Alcohol | — | Cyclopentanol | | | Cyclohexanol | | |
| | Hydroxy acrylate | H 136 | H 136 | H 136 | H 136 | H 136 | H 136 | H 136 |
| 10 | % DBTL s.o.s. ¹⁾ | 0.05 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 |
| | Coating hardness | | | | | | | |
| | Pendulum attenuation, König [swings] | | | | | | | |
| | after 5 h | 20 | 16 | 17 | 17 | 25 | 20 | 20 |
| | 7 d RT+15 h 60°C | 143 | 139 | 142 | 144 | 141 | 140 | 141 |
| 15 | Volatile organic constituents | | | | | | | |
| | VOC g/l | 512 | 498 | 485 | 485 | 505 | 496 | 486 |

Table 3: Improved VOC values relative to the prior art

| | | | | | | |
|----|--------------------------------------|-------------|------------------------------|-------------|-------------------------------|--|
| 20 | Coating composition | | | | | |
| | Coating material | 1 (compar.) | 8 | 9 | 10 | |
| | Polyisocyanate (Tab.1) | HI 100 | 11 | 14 | 16 | |
| | Alcohol | — | 3,3,5-Tri-methylcyclo-hexane | Norbor-neol | N-Methyl-4-hydroxy-piperidine | |
| 25 | Hydroxy acrylate | H 136 | H 136 | H 136 | H 136 | |
| | % DBTL s.o.s. ¹⁾ | 0.05 | 0.1 | 0.1 | — | |
| 30 | Coating hardness | | | | | |
| | Pendulum attenuation, König [swings] | | | | | |
| | after 5 h | 20 | 13 | 13 | 111 | |
| | 7 d RT+15 h 60°C | 143 | 144 | 140 | 130 | |
| 35 | Volatile organic constituents | | | | | |
| | VOC g/l | 512 | 495 | 492 | 477 | |

1) solid on solid

40

45

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Table 4: Improved drying times relative to low-viscosity products of the prior art (comparable VOC values)

| | | | | |
|--------------------------------------|-----------------|---------------|-------------------------------|------------------------------|
| Coating composition | | | | |
| Coating material | 12 (compar.) | 13 | 14 | 15 |
| Polyisocyanate (Tab.1) | 22 | 4 | 19 | 17 |
| Alcohol | 2-Ethyl-hexanol | Cyclo-hexanol | N-(2-Hydroxyethyl)-morpholine | N-Methyl-4-hydroxypiperidine |
| Coating hardness | | | | |
| Hydroxy acrylate | H 136 | H 136 | H 136 | H 136 |
| % DBTL s.o.s. | 0.1 | 0.1 | 0.1 | — |
| Pendulum attenuation, König [swings] | | | | |
| after 5 h | 10 | 18 | 25 | 112 |
| 7 d RT+15 h 60°C | 117 | 136 | 135 | 135 |
| Volatile organic constituents | | | | |
| VOC [g/l] | 477 | 476 | 494 | 475 |

- 20 Lumitol H 136: solids content = 70%, OHN = 135
 Basonat HI 100: HDI polyisocyanate, viscosity about 3000 mPas,
 solids content = 100%, NCO = 22%

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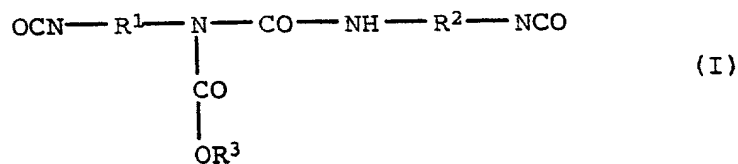
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We claim:

1. A diisocyanate of the formula (I)

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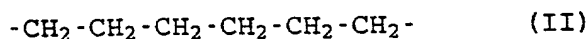


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in which the radicals have the following meanings:

R^1, R^2 : both radicals a radical of the formula (II)

15

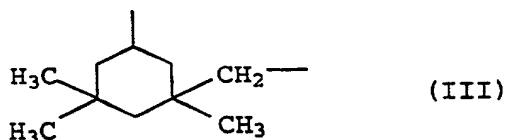


(diisocyanates Ia)

20

one radical a radical of the formula (II) and the other radical a radical of the formula (III)

25



(diisocyanates Ib)

30

both radicals a radical of the formula (III) (diisocyanates Ic),

35

R^3 : - a 5- or 6-membered cycloalkyl radical in which up to 3 hydrogen atoms may be substituted by C_1 - C_4 -alkyl radicals and one or two methylene units may be substituted by an oxygen atom and/or a tertiary nitrogen atom which additionally carries a C_1 - C_4 -alkyl radical, or

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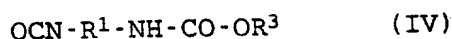
- a C_1 - C_4 -alkyl radical in which one hydrogen atom is substituted by a 5- or 6-membered cycloalkyl radical in which up to 3 hydrogen atoms may be substituted by C_1 - C_4 -alkyl radicals and one or two methylene units may be substituted by an oxygen atom and/or a tertiary nitrogen atom which additionally carries a C_1 - C_4 -alkyl radical; a pyrrolidone radical or a morpholine radical, where in the case of the two last-mentioned radicals the nitrogen atom is attached to the alkyl radical.

45

2. A diisocyanate as claimed in claim 1, in which the radical R^3 is derived from an alcohol selected from the group consisting of cyclohexanol, cyclohexanemethanol, cyclopentanol, cyclopentanemethanol, 3,3,5-trimethylcyclohexanol, menthol, norborneol, N-methyl-4-hydroxypiperidine, 4-(2-hydroxyethyl)-morpholine and 4-(2-hydroxyethyl)pyrrolidone.

3. A mixture comprising

- 10 - diisocyanates (Ia), (Ib) and/or (Ic),
- urethanes of the formula (IV)

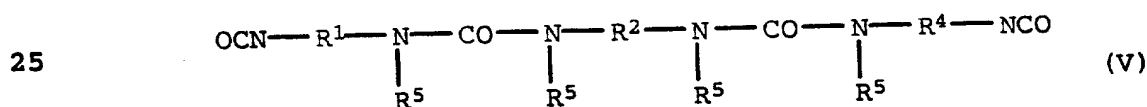


15 in which the radicals R^1 and R^3 may have the following meanings:

R^1 : a radical of the formula (II) or (III)

20 R^3 : the meaning indicated in claim 1;

- diisocyanates of the formula (V)



in which the radicals R^1 , R^2 , R^4 and R^5 may have the following meanings:

30 R^1 , R^2 , R^4 : the meaning indicated for R^1 in formula (I),

R^5 : 2 of the total of 4 radicals are hydrogen and the other two radicals are a radical of the formula (VI)



40 with the radicals R^5 having the same meaning being separated by the unit R^2 ; and

- isocyanurates composed of 3 molecules selected from the group consisting of isophorone diisocyanate and hexamethylene diisocyanate (monoisocyanurates VII).

45

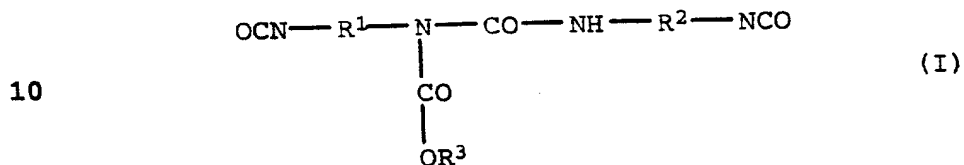
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4. A mixture as claimed in claim 3, where the weight ratio of diisocyanates (I) to monoisocyanurates (VII) is from 10:1 to 1:10.
- 5 5. A mixture as claimed in claim 3 or 4, where the proportion of isophorone diisocyanate or hexamethylene diisocyanate is less than 0.5% by weight.
- 10 6. A mixture as claimed in any of claims 3 to 5, where the sum of the proportions of the diisocyanates (Ia), (Ib), (Ic), (V), the urethane (IV) and the isocyanurate (VII) is from 10 to 100% by weight.
- 15 7. A process for preparing a mixture as claimed in any of claims 3 to 6, which comprises reacting
- (i) isophorone diisocyanate, hexamethylene diisocyanate or a mixture of these isocyanates in the presence of a catalyst with a
- 20 - 5- or 6-membered cycloaliphatic alcohol in which up to 3 hydrogen atoms attached to one carbon atom may be substituted by C₁-C₄-alkyl radicals and one or two methylene units may be substituted by an
- 25 oxygen atom and/or a tertiary nitrogen atom which additionally carries a C₁-C₄-alkyl radical, or
- C₁-C₄-alkyl alcohol in which one hydrogen atom attached to a carbon atom is substituted by a
- 30 5- or 6-membered cycloalkyl radical in which up to 3 hydrogen atoms may be substituted by C₁-C₄-alkyl radicals and one or two methylene units may be substituted by an oxygen atom and/or a tertiary nitrogen atom which additionally carries a
- 35 C₁-C₄-alkyl radical; a pyrrolidone radical or morpholine radical, where in the case of the two last-mentioned radicals the nitrogen atom is attached to the alkyl radical of the alcohol;
- 40 the molar ratio of said isocyanates to said monoalcohol being from 1.5:1 to 20:1,
- (ii) deactivating the catalyst and
- 45 (iii) removing any unreacted isocyanate.

Diisocyanates with allophanate groups derived from alicyclic alcohols

5 Abstract

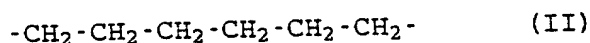
Diisocyanates of the formula (I)



in which the radicals have the following meaning:

15

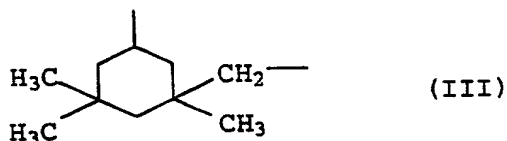
R^1, R^2 : - both radicals a radical of the formula (II)



20 (diisocyanates Ia)

- one radical a radical of the formula (II) and the other radical a radical of the formula (III)

25



(diisocyanates Ib)

30

- both radicals a radical of the formula (III) (diisocyanates Ic),

35 R^3 : - a 5- or 6-membered cycloalkyl radical in which up to 3 hydrogen atoms may be substituted by C_1 - C_4 -alkyl radicals and one or two methylene units may be substituted by an oxygen atom and/or a tertiary nitrogen atom which additionally carries a C_1 - C_4 -alkyl radical, or

40 - a C_1 - C_4 -alkyl radical in which one hydrogen atom is substituted by a 5- or 6-membered cycloalkyl radical in which up to 3 hydrogen atoms may be substituted by C_1 - C_4 -alkyl radicals and one or two methylene units may be substituted by an oxygen atom and/or a tertiary nitrogen atom which additionally carries a C_1 - C_4 -alkyl radical; a

45 pyrrolidone radical or a morpholine radical, where in the case of the two last-mentioned radicals the nitrogen atom is attached to the alkyl radical.

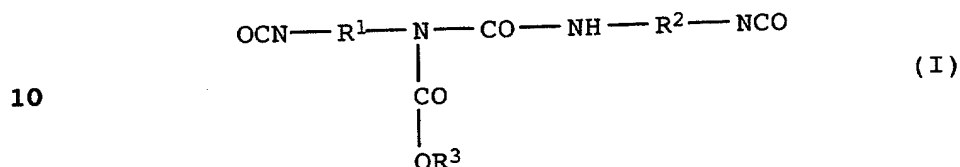
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THE FOLLOWING IS THE ENGLISH TRANSLATION OF THE
ANNEXES TO THE INTERNATIONAL PRELIMINARY
EXAMINATION REPORT : AMENDED SHEETS (Pages 14, 15, 16,
and 17).

We claim:

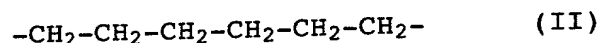
1. A mixture comprising

5 - diisocyanates of the formula (I)



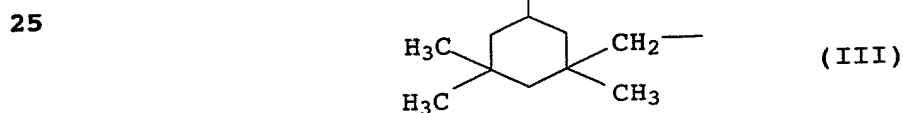
in which the radicals have the following meanings:

15 R^1, R^2 : both radicals a radical of the formula (II)



20 (diisocyanates Ia)

one radical of the formula (II) and the other radical a radical of the formula (III)



(diisocyanates Ib)

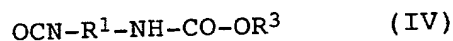
30 R^3 : - a 5- or 6-membered cycloalkyl radical in which up to 3 hydrogen atoms may be substituted by C_1 - C_4 -alkyl radicals and one or two methylene units may be substituted by an oxygen atom and/or a tertiary nitrogen atom which

35 additionally carries a C_1 - C_4 -alkyl radical, or

40 - a C_1 - C_4 -alkyl radical in which one hydrogen atom is substituted by a 5- or 6-membered cycloalkyl radical in which up to 3 hydrogen atoms may be substituted by C_1 - C_4 -alkyl radicals and one or two methylene units may be substituted by an oxygen atom and/or a tertiary nitrogen atom which additionally carries a C_1 - C_4 -alkyl radical; a pyrrolidone radical or a morpholine radical, where in the case of the two last-mentioned radicals the

45 nitrogen atom is attached to the alkyl radical

- urethanes of the formula (IV)

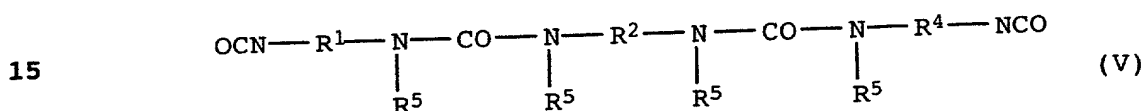


- 5 in which the radicals R^1 and R^3 may have the following meanings:

R^1 : a radical of the formula (II) or (III)

- 10 R^3 : the meaning indicated in claim 1;

- diisocyanates of the formula (V)



in which the radicals R^1 , R^2 , R^4 and R^5 may have the following meanings:

- 20 R^1 , R^2 , R^4 : the meaning indicated for R^1 in formula (I),

R^5 : 2 of the total of 4 radicals are hydrogen and the other two radicals are a radical of the formula (VI)



- 25 with the radicals R^5 having the same meaning being separated by the unit R^2 ; and

- 30 - isocyanurates composed of 3 molecules selected from the group consisting of isophorone diisocyanate and hexamethylene diisocyanate (monoisocyanurates VII),

- 35 where the weight ratio of diisocyanates (I) to monoisocyanurates (VII) is from 10:1 to 1:10.

- 40 2. A mixture as claimed in claim 1, in which the radical R^3 is derived from an alcohol selected from the group consisting of cyclohexanol, cyclohexanemethanol, cyclopentanol, cyclopentanemethanol, 3,3,5-trimethylcyclohexanol, menthol, norborneol, N-methyl-4-hydroxypiperidine, 4-(2-hydroxyethyl)-morpholine and 4-(2-hydroxyethyl)pyrrolidone.

45

3. A mixture as claimed in claim 1 or 2, where the proportion of isophorone diisocyanate or hexamethylene diisocyanate is less than 0.5% by weight.
- 5 4. A mixture as claimed in any of claims 1 to 3, where the sum of the proportions of the diisocyanates (Ia), (Ib), (Ic), (V), the urethane (IV) and the isocyanurate (VII) is from 10 to 100% by weight.
- 10 5. A process for preparing a mixture as claimed in any of claims 1 to 4, which comprises reacting
- (i) isophorone diisocyanate, hexamethylene diisocyanate or a mixture of these isocyanates in the presence of a catalyst with a
- 15
- 5- or 6-membered cycloaliphatic alcohol in which up to 3 hydrogen atoms attached to one carbon atom may be substituted by C₁-C₄-alkyl radicals and one or two methylene units may be substituted by an oxygen atom and/or a tertiary nitrogen atom which additionally carries a C₁-C₄-alkyl radical, or
- 20
- C₁-C₄-alkyl alcohol in which one hydrogen atom attached to a carbon atom is substituted by a 5- or 6-membered cycloalkyl radical in which up to 3 hydrogen atoms may be substituted by C₁-C₄-alkyl radicals and one or two methylene units may be substituted by an oxygen atom and/or a tertiary nitrogen atom which additionally carries a C₁-C₄-alkyl radical; a pyrrolidone radical or morpholine radical, where in the case of the two last-mentioned radicals the nitrogen atom is attached to the alkyl radical of the alcohol;
- 25
- 30
- 35 the molar ratio of said isocyanates to said monoalcohol being from 1.5:1 to 20:1,
- (ii) deactivating the catalyst and
- 40
- (iii) removing any unreacted isocyanate.
6. A process as claimed in claim 5, wherein the reaction is continued until the resulting reaction product after removing any unreacted isophorone diisocyanate or hexamethylene
- 45

diisocyanate still present has a viscosity of from 100 to 10,000 mPas measured in accordance with ISO 3219, Annex B.

- 5 7. A two-component coating composition comprising a compound which carries polyisocyanate-reactive groups (component A) and a mixture as claimed in claim 1 (I) (component B).
8. A method of coating articles which comprises
- 10 - preparing a coating composition as claimed in claim 7 by mixing components (A) and (B) and
- 15 - applying the coating composition in sheetlike manner to an article within 12 h of the preparation of said composition.
9. A coated article produced as claimed in claim 8.

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Declaration, Power of Attorney

Page 1 of 3

0050/048714

We (I), the undersigned inventor(s), hereby declare(s) that:

My residence, post office address and citizenship are as stated below next to my name,

We (I) believe that we are (I am) the original, first, and joint (sole) inventor(s) of the subject matter which is claimed and for which a patent is sought on the invention entitled

Diisocyanates with allophanate groups derived from alicyclic alcohols

the specification of which

☐ is attached hereto.

☐ was filed on _____ as

Application Serial No. _____

and amended on _____.

☒ was filed as PCT international application

Number PCT/EP 98/08383

on 18/12/1998

and was amended under PCT Article 19

on _____ (if applicable).

We (I) hereby state that we (I) have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

We (I) acknowledge the duty to disclose information known to be material to the patentability of this application as defined in Section 1.56 of Title 37 Code of Federal Regulations.

We (I) hereby claim foreign priority benefits under 35 U.S.C. § 119(a)-(d) or § 365(b) of any foreign application(s) for patent or inventor's certificate, or § 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed. Prior Foreign Application(s)

Application No.

Country

Day/Month/Year

Priority
Claimed

19801322.1

Germany

16 January 1998

☒ Yes ☐ No

We (I) hereby claim the benefit under Title 35, United States Codes, § 119(e) of any United States provisional application(s) listed below.

(Application Number)

(Filing Date)

(Application Number)

(Filing Date)

We (I) hereby claim the benefit under 35 U.S.C. § 120 of any United States application(s), or § 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of 35 U.S.C. § 112, I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR § 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application.

| Application Serial No. | Filing Date | Status (pending, patented, abandoned) |
|------------------------|-------------|---------------------------------------|
| _____ | _____ | _____ |
| _____ | _____ | _____ |
| _____ | _____ | _____ |
| _____ | _____ | _____ |

And we (I) hereby appoint:

Norman F. Oblon, Registration Number 24, 618;
 Marvin J. Spivak, Registration Number 24, 913;
 Gregory J. Maier, Registration Number 25, 599;
 William E. Beaumont, Registration Number 30, 996;
 Steven B. Kelber, Registration Number 30, 073;
 Jean-Paul Lavalleye, Registration Number 31, 451;
 Timothy R. Schwartz, Registration Number 32, 171;
 Stephen G. Baxter, Registration Number 32, 884;
 Richard L. Treanor, Registration Number 36, 379;
 Robert W. Hahl, Registration Number 33, 893;

our (my) attorneys, with full powers of substitution and revocation, to prosecute this application and to transact all business in the Patent Office connected therewith; and we (I) hereby request that all correspondence regarding this application be sent to the firm of **OBLON, SPIVAK, McCLELLAND, MAIER & NEUSTADT, P.C.**, whose Post Office Address is: Fourth Floor, 1755 Jefferson Davis Highway, Arlington, Virginia 22202.

We (I) declare that all statements made herein of our (my) own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

1-10

Bernd Bruchmann
NAME OF INVENTOR

Bernd Bruchmann
Signature of Inventor

Date

14/01/1999

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